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60 results found in the Worldwide database for:

bipyridyl in the title or abstract AND 1945:1974 as the publication date AND ICI as the applicant

Displaying selected publications

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ROYAUME DE BELGIQUE



MINISTRE DES AFFAIRES ECONOMIQUES

BREVET D'INVENTION

N° 799.255

Classif. Internat.: C 07 d

Mis en lecture le: 8-11-1973

Le Ministre des Affaires Economiques,

Vu la loi du 24 mai 1854 sur les brevets d'invention;

Vu la Convention d'Union pour la Protection de la Propriété Industrielle;

Vu le procès-verbal dressé le 8 mai 1973 à 15 h45

au Service de la Propriété industrielle;

ARRÊTE :

Article 1. — Il est délivré à la Sté dite : IMPERIAL CHEMICAL INDUSTRIES LIMITED,
Imperial Chemical House, Millbank, Londres SW1P 3JF, (Grande-Bretagne),
repr. par l'Office Kirkpatrick-G.C.Plucker à Bruxelles,

un brevet d'invention pour: Production de sels de 1,1'-dialkyl-4,4'-bipyridylum,

qu'elle déclare avoir fait l'objet de demandes de brevet déposées en Grande-Bretagne le 15 mai 1972, n° 22712/72, le 8 juin 1972, n° 26804/72 et le 4 septembre 1972, n° 40953/72.

Article 2. — Ce brevet lui est délivré sans examen préalable, à ses risques et périls, sans garantie soit de la réalité, de la nouveauté ou du mérite de l'invention, soit de l'exactitude de la description, et sans préjudice du droit des tiers.

Au présent arrêté demeurera joint un des doubles de la spécification de l'invention (mémoire descriptif et éventuellement dessins) signés par l'intéressé et déposés à l'appui de sa demande de brevet.

Bruxelles, le 8 novembre 1973.

PAR DÉLÉGATION SPÉCIALE

Le Directeur Général,

PATENT SPECIFICATION

(11) 1358 124

1358 124

- (21) Application No. 18629/72 (22) Filed 21 April 1972
 (23) Complete Specification filed 26 March 1973
 (44) Complete Specification published 26 June 1974
 (51) International Classification C07D 31/20
 (52) Index at acceptance
 C2C 1530 215 246 247 250 251 25Y 28X 290 29Y 30Y
 61X ZB
 (72) Inventors GEOFFREY JAMES MOORE and
 CHRISTOPHER TRIGGS



(54) MANUFACTURE OF 1,1'-DIMETHYL-4,4'-BIPYRIDILIUM SALTS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of 1,1' - dimethyl - 4,4' - bipyridylium salts.

Previously proposed methods for the production of a 4,4'-bipyridylium diquaternary salt by the quaternisation of the corresponding 4,4'-bipyridyl have involved the use of a quaternising agent providing, from a single molecule, not only (i) a quaternising group of atoms (which becomes attached to nitrogen in the bipyridylium salt formed) but also (ii) an atom or group of atoms which constitutes the anion of the bipyridylium salt.

Thus, for example, it is known to prepare 1,1' - dimethyl - 4,4' - bipyridylium dichloride from 4,4'-bipyridyl using methyl chloride as quaternising agent; alternatively chloroacetic acid may be used as quaternising agent in this process (as described in the specification of our UK Patent No. 1,135,682). Similarly, it is known that dimethyl sulphate may be used as quaternising agent in the preparation of 1,1' - dimethyl - 4,4' - bipyridylium dimethosulphate from 4,4'-bipyridyl.

It has hitherto been considered that the use of such highly reactive quaternising agents has been necessary in view of the relative difficulty of attaching the quaternary group to the second nitrogen atom of a mono-quaternary bipyridylium cation; thus, for example, the conversion of 1 - methyl - 4,4' - bipyridylium chloride (a mono-quaternary salt) into 1,1' - dimethyl - 4,4' - bipyridylium dichloride (the corresponding di-quaternary salt) is more difficult to accomplish than the conversion of 4,4'-bipyridyl into 1 - methyl - 4,4' - bipyridylium chloride.

We have now found that the production of 1,1' - dimethyl - 4,4' - bipyridylium salts

from 4,4'-bipyridyls may conveniently be carried out using methanol as the source of the quaternising methyl groups.

According to the present invention there is provided a method of preparing a 1,1' - dimethyl - 4,4' - bipyridylium salt which comprises interacting a 4,4'-bipyridyl with methanol in the presence of an acid containing an atom or group of atoms capable of constituting the anion of the 1,1' - dimethyl - 4,4' - bipyridylium salt.

The acid may be introduced as such or in the form of its salt with the 4,4'-bipyridyl. Thus, for example, hydrochloric acid may be introduced in the form of gaseous hydrogen chloride, in the form of a solution of hydrogen chloride in water, methanol or aqueous methanol, or in the form of a 4,4'-pyridyl hydrochloride.

While the process is especially applicable in the production of bipyridylium dichlorides (when hydrochloric acid is the acid providing the anion of the salt) other acids may be used to produce corresponding salts, for example hydrobromic acid, hydriodic acid, sulphuric acid or phosphoric acid may be used in the production of bipyridylium bromides, iodides, sulphates, and phosphates respectively.

While the process is especially applicable to the quaternisation of 4,4'-bipyridyl itself, quaternary salts of substituted 4,4'-bipyridyls may also be prepared by the process described herein, including 4,4'-bipyridyls substituted in one or both rings with one or more alkyl groups, especially one or more alkyl groups having one to four carbon atoms (for example 2,2' - dimethyl - 4,4' - bipyridyl and 2,6' - dimethyl - 4,4' - bipyridyl).

Bipyridylium mono-quaternary salts may also be used as starting materials in the quaternisation stage of the process described herein; for convenience the term "bipyridyl" is used herein to include a quaternisable 4,4'-bipyridylium mono-quaternary salt except where the context clearly precludes this.

The quaternisation process may be carried

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[54] **VARIABLE LIGHT TRANSMISSION
DEVICE**

[75] Inventor: **John Grahame Kenworthy**, Run-
corn, Cheshire, England

[73] Assignee: **Imperial Chemical Industries
Limited**, London, England

[22] Filed: **Nov. 22, 1971**

[21] Appl. No.: **200,776**

[52] U.S. Cl.**350/160 R**, 260/250 R, 260/294.9,
260/296 D

[51] Int. Cl.**G02f 1/36**, C07d 31/42

[58] Field of Search**350/160 R**; 260/294.9, 250 R,
260/296 D

[56] **References Cited**

UNITED STATES PATENTS

3,652,149 3/1972 Rogers.....350/160 R

Primary Examiner—Ronald L. Wibert

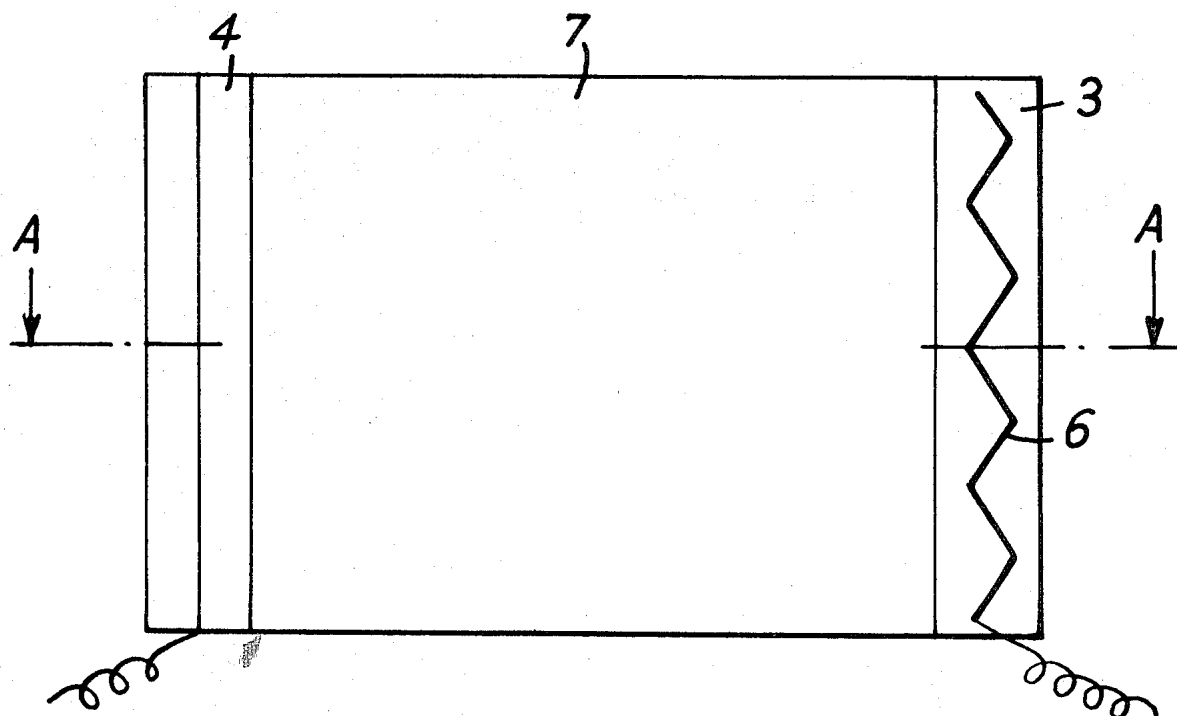
Assistant Examiner—V. P. McGraw

Attorney—Cushman, Darby & Cushman

[57] **ABSTRACT**

Device for light transmission control in response to electrical signals. A N-substituted p-cyanophenyl derivative of, for example, a bipyridyl is reversibly transformed between the cationic form (colorless) and radical (usually green) by application of potential between a transparent conducting electrode and a counter electrode.

7 Claims, 2 Drawing Figures



PATENT SPECIFICATION

(11) 1 340 006

1 340 006

NO DRAWINGS

- (21) Application No. 29584/71 (22) Filed 24 June 1971
 (23) Complete Specification filed 12 June 1972
 (44) Complete Specification published 5 Dec. 1973
 (51) International Classification C07D 31/02; A01N 9/02, 9/22
 (52) Index at acceptance
 C2C 173—197—288 215 246 247 250 251 25Y 28X 30Y
 43X 61X 69Y 776 ZB ZK
 A5E 1A3B 1A3C 1A5B3 1C14 1C15D2 1C15D3 1C15E
 1C15F2 1C7K 1C7L 1C7N 1C7P
 (72) Inventor GEOFFREY JAMES MOORE



(54) MANUFACTURE OF BIPYRIDYLS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of bipyridyls and particularly to a process for the manufacture of 4,4'-bipyridyls and 2,2'-bipyridyls from halopyridines.

It is well known, for example from U.K. Patent Specifications Nos. 956,854; 963,441; 1,016,541 and 1,030,154 that bipyridyls, notably 4,4'-bipyridyls, can be produced by reacting pyridine with a metal, for example sodium, magnesium or aluminium, to form a metal/pyridine interaction product, and subsequently oxidising this interaction product. Also, in copending U.K. Patent Application No. 39481/70 (Serial No. 1338399) we have described a process for the manufacture of bipyridyls which comprises heating pyridine with a halogen, a 4-halopyridine or a 1-(4-pyridyl)-pyridinium salt at a temperature of at least 150°C, an embodiment of this process comprising heating pyridine with chlorine or bromine at a temperature in excess of 150°C. optionally in the presence of a metal halide for example palladium bromide.

We have now found that bipyridyls can be produced by treating halopyridines with alcohols in the presence of palladium, conveniently at a temperature below 150°C.

According to the present invention we provide a process for the manufacture of 4,4'-bipyridyls and/or 2,2'-bipyridyls which comprises treating a 4-halopyridine or a 2-halopyridine with an alcohol in the presence of palladium and under basic conditions.

By the term "halopyridine" as used through-

out this specification we mean a halogenated pyridine containing one or more halogen atoms wherein the halogen is chlorine, bromine or iodine. The pyridine nucleus of the halopyridine may carry inert substituents, for example alkyl groups in any position not occupied by the halogen atom(s).

The process can be carried out simply by mixing a solution of the halopyridine in the alcohol containing palladium with a base at the desired temperature, for example from 0°C. to 150°C. Preferably the mixture is heated at a temperature of from 50°C. to 80°C. Conveniently the reaction can be carried out at the boiling point of the reaction mixture if desired under conditions of reflux.

The halopyridine may be generated *in situ* in the reaction mixture, for example by adding the hydrochloride of the halopyridine to a reaction mixture containing a strong base, for example an alkali-metal or alkaline earth metal hydroxide or an organic amine, for example an alkylamine such as triethylamine. An alcoholic solution of an alkali metal hydroxide is a convenient reaction medium and in this case the alcohol conveniently may be an alkanol, preferably an alkanol containing from one to six, especially from one to four carbon atoms, for example methanol.

The reaction medium may, and preferably does, contain water which may comprise an appreciable proportion of the reaction medium, for example up to 50% by weight of the reaction medium or even higher. The presence of water is believed to be beneficial because the water dissolves any alkali-metal halide formed and prevents fouling of the catalyst by this material.

The temperature at which the process of the invention is carried out can be for example from 0°C. to 150°C, although higher temperatures may be employed if the treatment is

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PATENT SPECIFICATION

(11) 1341427

1341427

NO DRAWINGS

(21) Application No. 19668/71 (22) Filed 9 June 1971

(23) Complete Specification filed 1 June 1972

(44) Complete Specification published 19 Dec. 1973

(51) International Classification C08F 27/08

(52) Index at acceptance

C3P 4D1A 4D3B3 4K4 4T2A 4T2D 4T2X

C4S 43Y 650 66Y 670 705 709 714 716 717 74Y 76Y

(72) Inventor JOHN GRAHAM ALLEN



(54) HYDROPHILIC POLYMER

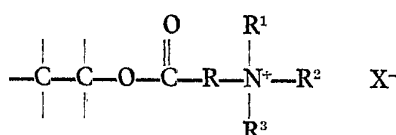
(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to hydrophilic polymers, some of which are photosensitive.

According to our invention there is provided a copolymer or blend of polymers containing (a) vinyl alcohol units and (b) units, derived from a vinyl ester, of structure I, below, the molar ratio of units (a):(b) being 15 1 to 100 to 1000 to 1 and the units (a) and (b) forming at least 80% of the blend or copolymer.

20 Where up to 20% of other units are present there may be other vinyl comonomer units, especially vinyl ester units. For example when a vinyl alcohol polymer is prepared by hydrolysis of polyvinyl acetate, up to 20% of the vinyl ester units may be left unhydrolysed.

Units (b) are defined by the structure I:—



I

30 where R is a divalent organic group such as methylene, poly(methylene), arylene e.g. benzyl or aralkylene, R^{1-3} are (same or different) organic substituents such as alkyl (preferably up to 3 carbon) or aryl, e.g. phenyl but are preferably part of a heterocyclic ring system based on the nitrogen atom and X^- is an anion.

35 If the nitrogen atom of units (b) is part of a heterocyclic ring system which is linked to a second nitrogen-containing heterocyclic ring system by a direct link or by an unsaturated

group such that a chain of conjugated unsaturation exists between the two nitrogen atoms, and provided the anion X^- is derived from a strong acid, then the resultant polymer is radiation sensitive, especially to ultraviolet radiation and to electron beams. Examples of such radiation sensitive polymers are those in which the nitrogen atom is part of 2,2'- or 4,4'-bipyridinium, 7,7'-diazapyrenium, 2,2'- or 4,4'-biquinolinium, 1,2-dipyridinium ethylene or 4 - (4'-pyridyl)pyridinium heterocyclic system. One nitrogen atom of such a system is linked to the polymer backbone and the other may be an unconnected tertiary nitrogen atom, or a quaternary nitrogen atom linked to a hydrocarbon group or to another strand of the same polymeric backbone to form cross-links.

Examples of corresponding anions are halides, especially chlorine, alkyl sulphate, bisulphate, tetrafluoroborate, silicofluoride, perchlorate, and fluoride.

60 Polymers according to our invention may be prepared by quaternisation of vinyl haloacetate units in a copolymer containing vinyl alcohol and vinyl haloacetate units or by similar treatment of a polymer blend containing such units. If, after quaternisation it is desired to replace the particular halide anion formed with another halide or a different (non halide) anion, this can be achieved by anion exchange.

70 The starting halogenated polymer containing vinyl haloacetate units may be obtained as such or may be made from poly vinyl alcohol by reaction with a haloacetyl halide. Preferably a copolymeric chain is employed, and to support photoreduction we have found a ratio of at least 1 vinyl alcohol to every 100 quaternisable haloacetate units to be desirable. Quaternised homopolymeric haloacetate may be mixed with poly vinyl alcohol to give a copolymer blend having a ratio of vinyl alcohol to quaternised vinyl haloacetate units such that a polymer according to our invention is formed.

The quaternisation reaction is usually car-

PATENT SPECIFICATION

(11) 1354322

1354322

- (21) Application No. 16006/71 (22) Filed 20 May 1971
(21) Application No. 28211/71 (22) Filed 16 June 1971
(23) Complete Specification filed 19 May 1972
(44) Complete Specification published 30 May 1974
(51) International Classification C23C 3/02
(52) Index at acceptance
C7F 1A 1B1B 2G 2L 2N 2U 2V 2Y 2Z6 3E 4A 4H 4J
4M 4N
(72) Inventors TIMOTHY DOUGLAS ANDREWS
ANTHONY GRAHAM MARSHALL LAST
IAN HODGSON and
ROBERT WILLIAM LOUCH



54) IMPROVEMENTS IN MAGNETIC INFORMATION CARRIERS

NOTICE OF AMENDMENT

SPECIFICATION NO 1354322

In accordance with an Order made by the Principal Examiner acting for the Comptroller-General dated 6 November 1975 under Section 26(2) Patent No 1354322 is revoked and in lieu thereof a Patent of Addition to No 1335962 has been granted to Imperial Chemical Industries Limited such Patent of Addition to bear the same number and date as the Patent so revoked.

The heading to the Specification has therefore been amended by adding the following clause:- (Patent of Addition to No 1335962 dated 5 November 1970).

THE PATENT OFFICE
12 December 1975

Bas 26753/23

PATENTS ACT 1949

SPECIFICATION NO 1354322

Reference has been directed, in pursuance of Section 9, subsection (1) of the Patents Act 1949, to Specification No 1335962.

THE PATENT OFFICE
17 June 1974

R 76263/1

35 to the sensitized state wherein the radiation sensitive material contains a component selected from:

- (1) neutral free radicals,
(2) radical cations, and
40 (3) neutral molecules, Z, derived from compounds containing dicationic units by two electron reduction, said dicationic compound being Z^{++} in the equation

chloride; polyvinylidene chloride; polycarbonates; polyimides; polysulphones; and linear polyesters such as polyethylene terephthalate and polyethylene - 1:2 - diphenoxyethane - 4:4' - dicarboxylate. The preferred support is a polyethylene terephthalate film.

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The present invention is particularly, although not exclusively, useful in the production of magnetic recording tapes, for example, audio, video, instrumentation and computer recording tapes. For such tapes the support

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SPECIFICATION AMENDED - SEE ATTACHED SLIP

PATENT SPECIFICATION

(11) 1377213

1377213

- (21) Application No. 12740/71 (22) Filed 3 May 1971
 (23) Complete Specification filed 3 May 1972
 (44) Complete Specification published 11 Dec. 1974
 (51) International Classification C07D 31/00
 (52) Index at acceptance
 C2C 1530 246 247 250 251 25Y 30Y 61X ZB
 (72) Inventors RAYMOND FREDERICK DALTON and
 DENNIS ALBERT DOWDEN and
 GEORGE HENRY LANG



(54) PREPARATION OF 2,2'-BIPYRIDYLS

- (71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to an improved process for the preparation of 2,2' - bipyridyls, intermediates for the manufacture of herbicides.
- According to the invention there is provided a process for the manufacture of 2,2' - bipyridyl or dialkyl - 2,2' - bipyridyls which comprises heating pyridine or an alkylpyridine at a temperature between 250°C and 500°C, and at a pressure above 200 p.s.i. gauge in the presence of one or more oxides of elements selected from groups Ib, IIa, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIa, VIIa and VIIIa of the periodic table, as given at page 411 of "Text-Book of Inorganic Chemistry" by J. R. Partington, fifth Edition published by Macmillan & Co.
- As pyridines there are mentioned especially pyridine itself, which is converted into 2,2' - bipyridyl, and also 2 -, 3- and 4 - methylpyridines which are converted into the appropriate dimethyl - 2,2' - bipyridyls.
- The oxides may be used as such or in the form of metal oxy-anion salts such as bismuth phosphomolybdate, cobalt aluminate, manganese chromate or nickel molybdate. The oxide or oxides may be used in powder form or as granules or pellets, and preferably they are supported on a medium which may be inert or is itself an oxide having a catalytic effect on this reaction, for example alumina, chromium oxide, kieselguhr or china clay. The preferred oxides are those of copper, titanium and tungsten.
- The temperature of the process is preferably a temperature above 300°C since with most of the metal oxides considerably higher production rates of bipyridyl are obtained at the higher temperatures. A particularly preferred range of temperature is between 300° and 450°C. The use of temperatures above 500°C leads to reduced yields of the required 2,2' - bipyridyl.
- The 2,2' - bipyridyl may be isolated from the reaction mixture by any conventional means, for example filtration to remove metal oxide, followed by fractional distillation of the filtrate. In the case when pyridine is used as the starting material the fraction collected at 135°—140°C/12 mm mercury pressure consists of 2:2' - bipyridyl, melting at 69°C.
- By the process of the invention, using cheap and readily available metal oxides as catalysts, rates of conversion of pyridines into bipyridyls are obtained which are in some cases at least comparable with those obtained by the use as catalyst of noble metals which are not readily available and are expensive.
- Specification Nos. 981383, 1000656 and 1026822 relate respectively to the use of rhodium, osmium or iridium, platinum or ruthenium, and rhenium catalysts in the preparation of bipyridyls by heating pyridines. In these specifications the use is disclosed of catalysts consisting of these metals supported on materials including metal oxides such as alumina. No claim is made in the present specification to the use as catalyst in the manufacture of bipyridyls from pyridine of these metal oxides when used as supports for metal catalysts as described in Specifications Nos. 981383, 1000656 and 1026822.
- The invention is illustrated but not limited by the following examples in which all parts and percentages are by weight unless otherwise stated.
- Example 1
- 4 parts of catalyst, as listed in the table below, and 25 parts of pyridine are heated in a sealed glass pressure tube at a temperature of about 340°C and the autogenous pressure of approximately 800 p.s.i.g. for 10 hours. After cooling the catalyst is removed by filtration to give a solution in pyridine of 2,2' - bipyridyl which is estimated by spectrophotometric analysis of the red complex formed with ferrous ion in pH 4.5 buffer solution.

PATENT SPECIFICATION

(11) 1339 081

NO DRAWINGS

1339 081

- (21) Application No. 5098/71 (22) Filed 22 Feb. 1971
 (23) Complete Specification filed 4 Feb. 1972
 (44) Complete Specification published 28 Nov. 1973
 (51) International Classification C07D 29/40 31/28 A01N 9/22
 (52) Index at acceptance

C2C 3A13A1A4 3A13A1C 3A13A1F3 3A13A1G 3A13A1L

- (72) Inventors JOHN FRANCIS CAIRNS and
 JOHN REGINALD CASE



(54) MANUFACTURE OF BIPYRIDYLUM SALTS

- (71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to the manufacture of 1,1' - di(hydroxyalkyl) - 4,4' - bipyridylum salts and particularly to a process for the manufacture of 1,1' - di(hydroxyalkyl) - 1,1',4,4' - tetrahydro - 4,4' - bipyridyls or salts thereof and their conversion into the corresponding 1,1' - disubstituted - 4,4' - bipyridylum salts which are useful herbicides.
- According to the present invention we provide a process for the manufacture of a 1,1' - di(hydroxyalkyl) - 1,1',4,4' - tetrahydro - 4,4' - bipyridyl or a salt thereof which comprises reacting a metal-pyridine interaction product with an alkylene oxide.
- It is preferred to carry out the reaction under substantially anhydrous conditions and the substantial absence of molecular oxygen is advantageous since oxygen tends to result in the formation of unwanted by-products.
- The reaction will usually be carried out in the presence of a liquid diluent medium, preferably one which is a solvent for the metal-pyridine interaction product. In this case an aprotic solvent is most suitable, for example liquid ammonia and polar aprotic organic solvents, for example dimethyl formamide, diglyme or pyridine, ammonia being the preferred solvent. The solvent preferably should be substantially anhydrous although a trace of water can be tolerated. The metal-pyridine interaction product conveniently may be employed in the form of a suspension in which it has been prepared, without first isolating it.
- The temperature at which the reaction is carried out is not critical and may vary over a wide range, for example from -120°C to 200°C , although the temperature may be dependent to some extent upon the solvent in which the reaction is carried out. Preferably the temperature is not greater than 150°C . Thus, for example, if liquid ammonia is employed as solvent the temperature of the reaction normally will not be above -33°C although higher temperatures may be employed if the reaction is carried out under superatmospheric pressure. The alkylene oxide usually will be employed in the liquid phase and temperatures in excess of the boiling point of the alkylene oxide normally will not be employed unless the reaction is carried out under superatmospheric pressure. Thus, for example, if ethylene oxide is employed at atmospheric pressure, the temperature normally will not exceed 10°C and if propylene oxide is employed the temperature normally will not exceed 35°C .
- The metal-pyridine interaction product can be produced by any known method, for example by reacting pyridine or a substituted pyridine with a dispersion of an alkali-metal, especially sodium, at a temperature of from 50°C to 120°C as described in UK Patent Specification No. 963,441; with a solution of an alkali-metal, especially sodium, in liquid ammonia as described in UK Patent Specification No. 1,030,154; with magnesium as described in UK Patent Specification No. 956,854; or with aluminium as described in UK Patent Specification No. 1,016,541. Production of a sodium-pyridine interaction product by reacting pyridine or an alkyl pyridine with a solution of sodium in liquid ammonia is advantageous in that the resulting solution of the sodium salt of a tetrahydro-4,4'-bipyridyl in liquid ammonia can be employed directly in the process of the present invention. Examples of substituents which may be present in the pyridine nucleus are alkyl, alkoxy, aryl, aryloxy, dialkylamino groups and halogen atoms.
- The alkylene oxide preferably contains from two to ten carbon atoms. We prefer to employ an alkylene oxide containing from two to four carbon atoms, especially ethylene oxide. The alkylene oxide is usually added

[Price 25p]

PATENT SPECIFICATION

(11) 1 328 382

NO DRAWINGS

1 328 382

- (21) Application No. 15960/70 (22) Filed 3 April 1970
 (61) Patent of Addition to No. 1 277 733 dated 12 June 1969
 (23) Complete Specification filed 19 April 1971
 (44) Complete Specification published 30 Aug. 1973
 (51) International Classification C07D 31/24, 99/02
 (52) Index at acceptance
 C2C 173—197—288 17X—186—272 17X—27X—287
 215 246 247 250 251 255 25Y 28X 290 29Y
 30Y 351 355 386 3A13A1A4 3A13A1C 3A13A1L
 43X 61X 635 675 791 UJ ZB
 (72) Inventor JOHN GERARD CAREY



(54) MANUFACTURE OF 1,1'-DISUBSTITUTED-4,4'-BIPYRIDYLIUM SALTS

- (71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 This invention relates to the manufacture of bipyridylium salts and more particularly to a process for the manufacture of 1,1' - disubstituted - 4,4' - bipyridylium salts which are useful herbicides.
- 15 In the specification of our U.K. Patent No. 1,277,733 we have described and claimed a process for the manufacture of 1,1' - disubstituted - 4,4' - bipyridylium salts wherein each of the substituents contains up to 10 carbon atoms which comprises reacting an N-substituted pyridinium salt with a cyanide under basic conditions and subsequently oxidising the resulting interaction product. It is stated therein that the cyanide is preferably an alkali metal cyanide, notably sodium cyanide.
- 25 We now provide a modification of the process described in the said specification wherein the cyanide is introduced in the form of hydrogen cyanide or a ketone cyanohydrin.
- 30 Thus according to the present invention we provide a process for the manufacture of a 1,1' - disubstituted - 4,4' - bipyridylium salt wherein each of the substituents contains up to 10 carbon atoms which comprises reacting an N-substituted pyridinium salt with a cyanide under basic conditions and subsequently oxidising the resulting interaction product, the said cyanide being introduced in the form of hydrogen cyanide or a ketone cyanohydrin.
- 40 We prefer to carry out the reaction in a medium which is a solvent for the N-substituted pyridinium salt. A wide variety of solvents may be employed. Examples of organic solvents which may be used are ethers and thioethers for example tetrahydrofuran, 1,2-dimethoxyethane, bis - (2 - methoxyethyl) ether, 1,4-dioxane and thiophene, ketones, for example acetone; hydrocarbons, for example benzene, toluene, xylene and hexane; organic bases, for example pyridine; halogenated hydrocarbons and particularly chlorinated hydrocarbons, for example chlorobenzene, chloroform, carbon tetrachloride and methylene dichloride; amides, particularly tertiary alkylamides, for example dimethyl formamide; organic amines, for example piperidine; heterocyclic bases for example pyridine; sulphoxides, for example dimethyl sulphoxide; sulphones, for example sulpholane; nitriles, for example acetonitrile; alcohols, for example ethanol; nitro compounds, for example nitropropane; and alkyl carbonates and sulphates, for example propylene carbonate and dimethyl sulphate. Polar aprotic solvents, especially dimethyl sulphoxide, are particularly suitable solvents since their use leads to high yields of the bipyridylium salts. Examples of suitable inorganic solvents are liquid ammonia and liquid hydrogen cyanide. Mixtures of solvents may be used if desired. We have found that liquid ammonia is an especially useful solvent; it may be used as the sole solvent or in admixture with others, notably organic solvents.
- 75 The reaction preferably is carried out under substantially anhydrous conditions, although up to 10 molar per cent of water has little or no effect on the yield of the interaction product.
- 80 The temperature at which the reaction is carried out is not critical although it may depend to some extent upon the particular solvent employed. In general, however, temperatures of from 0°C. to 120°C. are suitable.

PATENT SPECIFICATION

(11) 1313791

1313791

NO DRAWINGS

- (21) Application No. 10679/70 (22) Filed 5 March 1970
 (61) Patent of Addition to No. 1 277 733 dated 12 June 1969
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 (51) International Classification C07D 31/28
 (52) Index at acceptance
 C2C 3A13A1A4 3A13A1C 3A13A1L
 (72) Inventors JOHN EDWARD COLCHESTER and THOMAS BLUNDELL



(54) MANUFACTURE OF 1,1'-DISUBSTITUTED-4,4'-BIPYRIDYLUM SALTS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of 1,1'-disubstituted-4,4'-bipyridylum salts which are useful herbicides, and particularly to a process for the manufacture of 1,1'-di(hydroxyalkyl)-4,4'-bipyridylum salts.

In our British Patent No. 1277733 we have described and claimed a process for the manufacture of 1,1'-disubstituted-4,4'-bipyridylum salts wherein each of the substituents contains up to 10 carbon atoms which comprises reacting an N-substituted pyridinium salt with a cyanide under basic conditions and subsequently oxidising the resulting interacting product.

In the copending Application the invention is particularly described in respect of 1,1'-disubstituted-4,4'-bipyridylum salts wherein the substituents are hydrocarbon groups, particularly alkyl or aryl groups, or carbamido-alkyl groups, and we have now realised that 1,1'-di(hydroxyalkyl)-4,4'-bipyridylum salts can be produced by the process.

According to the present invention we provide a process for the manufacture of a 1,1'-di(hydroxyalkyl)-4,4'-bipyridylum salt wherein each of the hydroxyalkyl substituents contains up to 10 carbon atoms which comprises reacting an N-hydroxyalkyl pyridinium salt with a cyanide under basic conditions and subsequently oxidising the resulting interaction product. The cyanide conveniently is an alkali metal cyanide, notably sodium cyanide, although other cyanides may be used, if desired.

The reaction can be carried out simply by mixing the reagents and heating the mixture if necessary, but we prefer to carry out the

reaction in a solvent for the N-hydroxyalkyl pyridinium salt. A suitable solvent is an aqueous medium, e.g., water although a wide variety of organic solvents may be employed. Examples of organic solvents which may be used are ethers and thioethers for example tetrahydrofuran, 1,2-dimethoxyethane, bis-(2-methoxyethyl)ether, 1,4-dioxane and thiophene; organic bases, for example pyridine; amides, particularly tertiary alkylamides, for example dimethyl formamide; sulphoxides, for example dimethyl sulphoxide; sulphones, for example sulfolane; nitriles, for example acetonitrile; alcohols, for example ethanol; nitro compounds, for example nitropropane; and alkyl carbonates and sulphates, for example propylene carbonate and dimethyl sulphate. Polar aprotic solvents, especially dimethyl sulphoxide, are particularly suitable solvents since their use leads to high yields of the bipyridylum salts. Mixtures of solvents may be used if desired.

Another particularly suitable solvent is a mixture of water and an alcohol which is miscible with water. The alcohol in such mixtures may be in particular in aliphatic alcohol, especially an alkanol, although aromatic or cycloaliphatic alcohols may be used if desired. We prefer to employ alcohols of boiling point less than 100°C at atmospheric pressure, especially methanol or ethanol. Mixtures of two or more alcohols with water may be used if desired.

The amounts of water and alcohol in the mixture may vary within wide limits but we have found that for any particular alcohol/water mixture there exists a range of water contents in which particularly good yields of the reaction product, and hence of the bipyridylum salt, are obtained. Although the preferred range of water contents may vary slightly for different alcohols we have found that in general mixtures are preferred which contain from 5% to 65% by volume and especially from 20% to 50% by volume of

[Price 25p]

PATENT SPECIFICATION

(11) 1276253

NO DRAWINGS

- (21) Application No. 8481/70 (22) Filed 23 Feb. 1970
 (23) Complete Specification filed 19 April 1971
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 (51) International Classification C07D 31/26//A01N 9/22
 (52) Index at acceptance
 C2C 173—197—288 215 247 250 251 25Y 28X 313 31Y
 337 440 61X 791 79Y ZB
 (72) Inventor ROY DENNIS BOWDEN



(54) HALOGENATED HETEROCYCLIC COMPOUNDS

- (71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1., a British Company do hereby declare the invention, for which we
 5 pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
 This invention relates to chloropyridine derivatives and more particularly to novel
 10 chloro-derivatives of 2,3'- and 2,4'-bipyridyl.
 According to the present invention there are provided the novel compounds octachloro-2,3'-bipyridyl and octachloro-2,4'-bipyridyl.
 15 According to a further aspect of the present invention there is provided a process for the manufacture of octachloro-2,3'-bipyridyl or octachloro-2,4'-bipyridyl which comprises interacting 2,3'-bipyridyl or 2,4'-bipyridyl
 20 respectively with chlorine in the vapour-phase at an elevated temperature.
 The reaction between 2,3'-bipyridyl or 2,4'-bipyridyl and chlorine may be carried out over a wide range of temperature, preferably
 25 in the range from 400°C to 600°C. A temperature in the range from 500°C to 600°C is especially preferred.
 It is preferred to preheat separately the feed of chlorine and the feed of the bipyridyl.
 30 The reactants may be diluted with inorganic diluents, for example nitrogen and/or steam, or with organic diluents, preferably inert towards chlorine, for example carbon tetrachloride. When a gaseous or volatile diluent
 35 is used the bipyridyl starting material may be vaporised in the stream of diluent vapour which serves as a carrier gas; when a liquid diluent is used, the bipyridyl starting material may be dissolved in the liquid diluent and the resulting solution may then be vaporised
 40 as a whole.
 In general, it is preferred to use at least 2 moles of chlorine, and especially at least 6 moles (for example 10 to 40 moles) of chlorine, for each mole of the bipyridyl starting material. When using a diluent which is reactive towards chlorine, for example chloroform, an appropriate additional amount of chlorine
 45 may be used to allow for that consumed by reaction with the diluent.
 The reaction may be carried out in the absence of a catalyst, but a catalyst may be present if desired, for example a porous material comprising silica, alumina, (a mixture or combination of silica and alumina, or carbon.
 50 Convenient contact times of the mixture in the reaction zone are, for example, between 2 seconds and 20 seconds, though higher or lower contact times may also be used.
 The desired octachloro-bipyridyls may be isolated from the reaction products by conventional techniques, for example by fractional distillation, fractional crystallization, solvent extraction or a combination of such techniques.
 55 Octachloro-2,3'-bipyridyl and octachloro-2,4'-bipyridyl are useful as herbicides. Thus the invention further provides a herbicidal composition containing as an active ingredient octachloro-2,3'-bipyridyl or octachloro-2,4'-bipyridyl in association with a carrier.
 The carrier may comprise a solid diluent in powdered form, for example powdered kaolin, bentonite or talc. Alternatively the carrier may comprise a liquid diluent, for
 60 example water or petroleum oils.
 The herbicidal compositions may further comprise a surface-active agent, which may be of the cationic, anionic or non-ionic type. Suitable agents of the cationic type include
 65 for example quarternary ammonium compounds, for example cetyltrimethyl ammonium bromide. Suitable agents of the anionic type included for example soaps, salts of aliphatic monoesters of sulphuric acid, for example
 70 sodium lauryl sulphate; and salts of sulphonated aromatic compounds, for example sodium dodecylbenesulphonate, sodium, calcium, and ammonium lignosulphonate, butylnaphthalene-sulphonate, and a mixture of the sodium salts
 75 of diisopropyl- and triisopropyl-naphthalene-sulphonic acid. Suitable agents of the non-ionic type include, for example, the condensation products of ethylene oxide with fatty alcohols such as oleyl alcohol and cetyl
 80 alcohol, or with alkyl phenols such as octyl-

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NO DRAWINGS

- (21) Application No. 6857/70 (22) Filed 12 Feb. 1970
 (23) Complete Specification filed 19 April 1971
 (45) Complete Specification published 16 Aug. 1972
 (51) International Classification C07C 17/42, 25/14
 (52) Index at acceptance
 C2C 220 226 227 22Y 303 313 31Y 339 561 56Y 73Y 776
 HF
 (72) Inventors ERIC ILLINGWORTH and ALEC FLEMING



(54) STABILISATION OF CHLORINATED HYDROCARBONS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we

5 pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a method of stabilising chlorinated hydrocarbons which are prone to thermally induced polymerisation, particularly benzyl chloride, against the effects of applied heat.

15 Chlorination of certain hydrocarbons for example chlorination of toluene to produce benzyl chloride, benzal chloride and benzotrichloride, and subsequent distillation of the products is commonly carried out in essentially non-metallic apparatus in order to minimise

20 catalysis of unwanted polymerisation by metals. Despite these precautions considerable polymerisation normally occurs, especially at the distillation stage, resulting in serious deterioration in fractionation efficiency and

25 product quality and eventually in blockage of the fractionation column which then has to be dismantled and repacked.

30 According to the invention a method of stabilising against the effect of applied heat a chlorinated hydrocarbon which is prone to thermally induced polymerisation comprises applying said heat thereto in the presence of a tertiary amine having a boiling point of at least 230°C at 760 mm. Hg pressure.

35 Desirably the tertiary amine used in the invention should be capable of sequestering metal ions, particularly iron ions.

40 Examples of tertiary amines suitable for use in the invention are quinoline, 4,4'-bipyridyl and especially 2,2'-bipyridyl.

45 In a preferred embodiment the invention provides a means of inhibiting polymerisation during continuous or batch-wise distillation of a chlorinated hydrocarbon, particularly benzyl chloride.

The apparatus used in carrying out the invention may be of conventional type, for example, glass, silica, porcelain or non-ferrous

[Price 25p]

metals and may include a fractionating column.

The amount of tertiary amine used need 50 only be very small. For example when 2,2'-bipyridyl is used the proportion need only be from 1 to 20 parts per million parts by weight of the chlorinated hydrocarbon. Even in such small quantities 2,2'-bipyridyl effectively in- 55 hibits decomposition and polymerisation of chlorinated hydrocarbons e.g. benzyl chloride during distillation. Larger amounts than this can be used if desired, however, without apparent disadvantage. Being of very low volatility the tertiary amine does not pass through conventional fractionation equipment with the chlorinated hydrocarbon, and according to its point of entry it may appear in a 60 bottoms fraction or still residue.

65 Conveniently the tertiary amine may be added to the chlorinated hydrocarbon in the form of a solution in a liquid which forms a component of the distillation mixture, for example in toluene when it is desired to stabilise benzyl chloride during distillation of a crude product obtained by chlorination of toluene.

70 It is advantageous to supply the tertiary amine in such a way as to promote thorough dispersion throughout the chlorinated hydrocarbon which is to be stabilised. Thus for example in the distillation of crude benzyl chloride a solution of the tertiary amine (e.g. in toluene) may be fed into and mixed with the crude product at or immediately prior to the commencement of distillation. 75

80 The invention, particularly as applied to the stabilisation of benzyl chloride by 2,2'-bipyridyl enables distillation vessels and fractionating columns to be kept free from blockage by polymers and decomposition products during long periods of time and thereby provides a method of fractionation which is economically advantageous over presently operated methods. 85

90 The invention is illustrated but not limited by the following Example:—

The following table summarises test runs in which (as a control experiment) no stabiliser was used and in which 2,2'-bipyridyl and 95 quinoline were used as stabilisers the quantity

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(11) 1 308 561

1 308 561

NO DRAWINGS

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(51) International Classification C07D 31/02

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290 29Y 30Y 342 34Y 3A13A1A4 3A13A1C 579

580 589 596 61X 63X 791 79Y KW ZB

(72) Inventors JOHN BEACHAM and JOHN GERARD CAREY

(19)



(54) MANUFACTURE OF 1,1'-DISUBSTITUTED-4,4'-BIPYRIDYLIUM SALTS AND RELATED COMPOUNDS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of heterocyclic bases and particularly to a process for the manufacture of 1,1' - disubstituted - 4,4' - bipyridylium cation radicals which are readily oxidised to 1,1' - disubstituted - 4,4' - bipyridylium salts which are useful herbicides.

It is known that 1,1' - disubstituted - 4,4' - bipyridylium salts can be prepared by oxidation of the corresponding 1,1' - disubstituted - 1,1' - dihydro - 4,4' - bipyridyl. Thus in U.K. Patent Specification No. 1,269,353 there is described and claimed a process for the manufacture of 1,1'-disubstituted bipyridylium salts which comprises treating the corresponding 1,1' - disubstituted - 1,1' - dihydro-bipyridyl with oxygen or an oxidising agent which is an electron acceptor and which has a redox potential in water more positive than -0.50 volt as compared with the saturated calomel electrode. The reaction may be carried out in the presence of a solvent for the dihydrobipyridyl and a variety of inorganic and organic oxidising agents may be employed, for example metal salts, inorganic oxyacid anhydrides and quinones.

Also, in U.K. Patent Specification No. 1,277,733 we have described and claimed a process for the manufacture of 1,1' - disubstituted - 4,4' - bipyridylium salts wherein each of the substituents contains up to 10 carbon atoms which comprises reacting an N-substituted pyridinium salt with a cyanide under basic conditions and subsequently oxidising the resulting interaction product. The cyanide is preferably an alkali metal cyanide,

notably sodium cyanide. It is further described that the interaction product derived from the pyridinium salt and the cyanide is readily oxidised to the corresponding bipyridylium salt by treatment with air or with an oxidising agent, and that oxidation may be carried out prior to or subsequent to isolation of the intermediate interaction product. It is usually more convenient, as described, to isolate the intermediate reaction product prior to oxidising it and a technique for doing this is by solvent-extraction using an organic solvent, for example an aromatic hydrocarbon and notably toluene. The interaction product is in fact a 1,1' - disubstituted - 1,1' - dihydro - 4,4' - bipyridyl.

Oxidation of 1,1' - disubstituted dihydro-bipyridyls is in fact a two-stage process wherein the dihydrobipyridyl is firstly oxidised to the 1,1' - disubstituted - 4,4' - bipyridylium cation radical which is further oxidised in a second stage to the 1,1' - disubstituted - 4,4' - bipyridylium dication. We have now devised a particularly convenient method for converting dihydrobipyridyls into bipyridylium cation radicals.

According to the present invention we provide a process for the manufacture of a solution of a 1,1' - disubstituted - 4,4' - bipyridylium cation radical which comprises mixing a 1,1' - disubstituted - 1,1' - dihydro-4,4' - bipyridyl with a solution of a 1,1' - disubstituted - 4,4' - bipyridylium salt to form the solution of a 1,1' - disubstituted - 4,4' - bipyridylium cation radical. Usually, but not necessarily, the 1- and 1'-substituents of the bipyridylium salt will be the same as the 1- and 1'-substituents of the dihydrobipyridyl with which it is mixed, and normally the bipyridylium salt will be employed in the form of its aqueous solution. The 1,1' - disubstituted - 4,4' - bipyridylium cation radical is readily oxidised to a 1,1' - disubstituted-4,4' - bipyridylium salt.

PATENT SPECIFICATION

(11) 1335 962

1335 962

NO DRAWINGS

- (21) Application No. 57862/69 (22) Filed 26 Nov. 1969
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 (51) International Classification C23C 3/02
 (52) Index at acceptance

C7F 1A 1B1B 2G 2H 2L 2N 2P 2U 2V 2Y 3E 4J 4N
 G2C CX

(72) Inventor TIMOTHY DOUGLAS ANDREWS



(54) DEPOSITION OF METALS ONTO ORGANIC MATERIALS

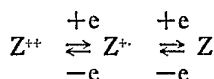
(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London S.W.1. a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

General Principles of the Invention

This invention relates to a metal deposition process, and in particular to a process for the deposition of metals onto organic materials.

According to the invention metal is deposited, by contacting the substrate with an electroless plating solution, in or on a substrate containing or consisting of an organic compound selected from

- (1) radical cations $Z^{\cdot+}$, and
- (2) neutral molecules, Z , derived from compounds containing dicationic units by two electron reduction, said dicationic compound being Z^{++} in the equation



and in which Z^{++} is the normally stable oxidation state of the molecule in aqueous media;

said dicationic compound being a salt containing in the molecule nitrogen atoms, at least two of which are quaternised and are also contained in linked at least partially aromatic rings, the link providing a chain of conjugated unsaturation between the nitrogen atoms. For convenience the organic compound identified above will be referred to as the "active component".

The term "electroless plating solution" is used in its normal meaning in metal plating technology, that is, a solution containing a metal salt and a reducing agent capable of depositing metal without the external application of an electrical potential. This deposition occurs in a way which has not yet been satisfactorily explained, merely requiring some form of activation of the receiving surface, e.g. by abrasion or by an initial deposit of a trace of metal. The present invention resides in discovery that the above defined organic compounds are capable of causing metal to be deposited from the electroless plating solution. Once a trace of metal has been deposited on the organic material, the metal so deposited is capable of catalysing further deposition of the same or a different metal from the appropriate solution, and a layer of metal can be built up.

In a modification of the invention, the substrate containing or consisting of organic compounds selected from radical cations or a neutral compound as defined above is contacted first with sensitizer comprising a solution of a compound of a metal of the platinum group (Ru, Rh, Pd, Os, Ir, Pt) silver or gold and subsequently with the electroless plating solution. This technique is preferred in some cases where the straight forward electroless plating without the sensitizer requires too long a processing time or too high a temperature for convenience.

The Substrate

The active component of the substrate is the radical cation or defined neutral compound. The active component may itself form the substrate or a support may be

PATENT SPECIFICATION

(11)

1 324 644

NO DRAWINGS

1 324 644

(21) Application No. 53506/69 (22) Filed 31 Oct. 1969

(23) Complete Specification filed 3 Dec. 1970

(44) Complete Specification published 25 July 1973

(51) International Classification C07D 31/02

(52) Index at acceptance

C2C 173—197—288 215 246 247 250 251 25Y 28X 30Y

61X 791 79Y ZB

(72) Inventors ROY DENNIS BOWDEN and THOMAS SEATON

(19)



(54) PROCESS FOR THE MANUFACTURE OF 4,4'-BIPYRIDYLS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the manufacture of 4,4'-bipyridyls.

According to the present invention we provide a process for the manufacture of a 4,4'-bipyridyl which comprises interacting a corresponding substituted pyridine derivative in the liquid phase with ammonia or ammonium ions in the presence of molecular oxygen, the said pyridine derivative being a 4-(4-pyridyl)-2,6-disubstituted tetrahydropyran (or tetrahydrothiopyran) wherein each of the 2- and 6-substituents is an alkoxy group or an alkylthio group, or a 3-(4-pyridyl)-1,1,5,5-tetrasubstituted pentane wherein each substituent is an alkoxy group or an alkylthio group.

The alkoxy or alkylthio groups of the tetrahydropyran derivative and the pentane derivative preferably contain from 1 to 6 carbon atoms and especially are methoxy (methylthio) or ethoxy (ethylthio) groups.

It is preferred to carry out the reaction under conditions such that the ammonia is present predominantly as an ammonium salt rather than as free ammonia; the pH range from 1 to 7 is especially preferred.

Ammonium ions may be introduced as such or may be generated *in situ*. It is preferred to introduce ammonium ions in the form of an ammonium salt; suitable ammonium salts include the salts of aliphatic carboxylic acids, for example ammonium acetate, and the salts of mineral acids, for example ammonium sulphate and ammonium nitrate. Alternatively, gaseous ammonia or a solution of ammonia may be introduced into the reaction mixture. Amides hydrolysable to form ammonium ions, for example formamide or urea, may also be employed.

It is preferred to use at least one mole of ammonium ion or ammonia for each mole of the substituted pyridine derivative. The concentration of ammonium ions is preferably at least 0.01 gram-ions per litre, for example in the range 0.01 to 2.0 gram-ions per litre.

The reaction is preferably carried out in a medium which comprises water and/or an organic solvent; mixtures of water with one or more organic solvents are especially suitable. A wide range of organic solvents may be used but it is preferred to use an alkanolic acid containing up to 6 carbon atoms in the alkyl group, for example acetic acid or propionic acid. It is especially preferred to use aqueous acetic acid containing, for example, from 2% to 50% by weight of acetic acid.

When an ammonium salt is employed in the reaction, the acidity of the reaction mixture may be derived from the ammonium salt but additional acid is often required; if so it is conveniently the acid corresponding to the ammonium salt employed. Thus in one embodiment of the invention, aqueous acetic acid is used as the reaction medium and ammonium acetate is the source of ammonium ions.

The reaction may be carried out over a wide range of temperature and pressure, depending partly upon the particular reactants and reaction medium. In general, it is preferred to use temperatures in the range from 15°C to 150°C, especially in the range from 80°C to 130°C.

Preferably, the reaction is carried out at a pressure in the range from 1 to 30 atmospheres, for example in the range from 1 to 20 atmospheres; higher pressures, for example up to 50 atmospheres, may however be employed. (Pressures are expressed throughout as atmospheres absolute).

The partial pressure of oxygen is preferably in the range from 0.1 to 20 atmospheres; it is especially preferred to use an oxygen partial pressure of at least 0.5 atmosphere,

PATENT SPECIFICATION

(11) 1270863

1270863

NO DRAWINGS

- (21) Application No. 41516/69 (22) Filed 20 Aug. 1969
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 (52) Index at acceptance

C2C 173—197—288 215 246 247 250 251 25Y 28X 290
 29Y 30Y 323 32Y 342 34Y 351 355 366 61X 62X
 650 791 KK ZB

(72) Inventor JOHN GERARD CAREY



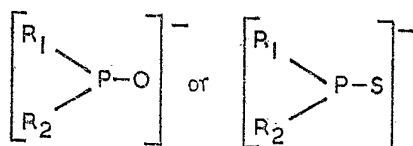
(54) BIPYRIDYLIUM SALTS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of bipyridylium salts and particularly to a process for the manufacture of 1,1' - di - substituted - 4,4' - bipyridylium salts which are useful herbicides.

According to the present invention we provide a process for the preparation of 1,1' - disubstituted - 4,4' - bipyridylium salts wherein each of the substituents contains up to 10 carbon atoms which comprises reacting the corresponding N - substituted pyridinium salt under basic conditions with anions containing the structure $>P-O^-$ or $>P-S^-$, and subsequently oxidising the resulting interaction product to give a 1,1' - disubstituted - 4,4' - bipyridylium salt.

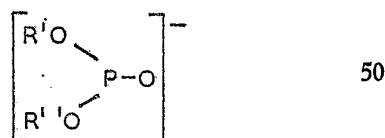
The anions may, for example, have the formula



wherein R_1 and R_2 may be the same or different and each is an alkyl (for example of up to 22 carbon atoms), aryl (for example phenyl), alkaryl or aralkyl group or a group of the formula $R'O-$, $R'S-$, R'_2N or R'_2P wherein R' is a hydrocarbon radical, for example an alkyl, aryl, alkaryl or aralkyl group and in addition R' may be a hydrogen atom in the group R'_2N- , and wherein if each of R_1 and R_2 is a group of the formula

$R'O-$, $R'S$, R'_2N or R'_2P , then the R' groups when taken together may form a cyclic structure. R' is preferably a phenyl group or an alkyl group containing from 1 to 8 carbon atoms, for example an ethyl group.

In a particular embodiment of the invention, the N - substituted pyridinium salt is reacted under basic conditions with a phosphonate. Preferably, the phosphonate is one which gives rise to a phosphonate anion of the formula



wherein R' and R'' , which may be the same or different, are alkyl groups, aryl groups or aralkyl groups or are groups which form part of a cyclic system.

A wide variety of cations may be associated with the anions; the cations conveniently may be alkali metal cations. Thus sodium or potassium salts may be employed, for example sodium or potassium dialkylphosphonate, sodium or potassium dialkylthiophosphonates or sodium or potassium secondary phosphine oxides or phosphinites. The anions may be added in association with cations as above or they may be formed *in situ* if desired. Thus there may be employed compounds of phosphorus which give rise to the desired anions under the conditions of the reaction. Phosphorus itself may be employed under appropriate conditions, for example in the presence of an alkali metal hydroxide. Examples of anions which may be used are dialkyl or diaryl phosphinites and thiophosphinites and dialkyl or diaryl phosphonates and thiophosphonates, and these may be formed *in situ* from the corresponding dialkyl or diaryl phos-

PATENT SPECIFICATION

(11) 1310516

1310516

NO DRAWINGS

- (21) Application No. 34414/69 (22) Filed 8 July 1969
 (23) Complete Specification filed 22 June 1970
 (44) Complete Specification published 21 March 1973
 (51) International Classification C07D 31/00, 57/00, 99/04
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 C2C 172—194—284 173—197—288 178—196—274
 215 246 247 250 251 253 25Y 28X 305 30Y 321
 32Y 3A13A3A4 3A13A3B1 3A13A3K 456 45Y
 61X 620 650 65Y NL ZB
 (72) Inventor ROY DENNIS BOWDEN

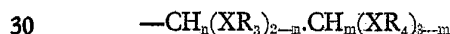


(54) MANUFACTURE OF PYRIDINE DERIVATIVES

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of pyridine derivatives and particularly to a process for use in the manufacture of bipyridyls from substituted pyridines.

According to the present invention we provide a process for the manufacture of bipyridyls which comprises reacting a substituted pyridine in the liquid phase with ammonia at a temperature of from 200° C to 450° C and converting any pyridyl piperidine so formed into a bipyridyl, the substituted pyridine being a 2 - (pyridyl) - tetrahydropyran or a 2 - (pyridyl) - tetrahydrothiopyran, a 4 - (pyridyl) - tetrahydropyran, or a 4 - (pyridyl) - tetrahydrothiopyran, or a substituted pyridine wherein the substituent is a group of the structural formula $-\text{C}(\text{R})(\text{R}_1)(\text{R}_2)$ wherein R represents a hydrogen atom, a halogen atom, a hydroxy group, an alkoxy group or an amino group, and R_1 and R_2 each represents a group of the general formula



wherein X represents an atom of oxygen or sulphur, n is 0, 1 or 2 and m is 1 or 2, and R_3 and R_4 each represents a hydrogen atom or an alkyl, alkenyl, aryl, alkaryl, aralkyl or cycloaliphatic group. In the pyridine derivatives (including the pyridyl tetrahydropyrans and pyridyl tetrahydrothiopyrans), the substituent may be in the 2, 3 or 4 position in the pyridine nucleus.

The reaction may be carried out in the presence of hydrogen and is preferably carried out at superatmospheric pressure. Especially,

pressures over 10 atmospheres may be employed.

The substituted pyridine starting material in the liquid phase is heated with ammonia at a temperature of from 200° C to 450° C, preferably 200° C to 350° C, usually in the presence of a hydrogenation/dehydrogenation catalyst. Suitable catalysts are the transition metals and their oxides and salts, for example the platinum metals, the Raney metals, nickel, cobalt, copper, chromium and copper chromite. The salts may be, for example, sulphides, and the catalyst may be unsupported or supported, for example, nickel supported on kieselguhr.

The substituted pyridine starting material may be employed in the bulk form or it may be in the form of a solution in a solvent which is preferably inert to the reactants. If a solvent is employed it is preferably, but not necessarily, of a sufficiently high boiling point that it remains in the liquid phase throughout the reaction. Examples of suitable organic solvents are ethers and thioethers for example tetrahydrofuran, 1,2-dimethylethane, bis-(2-methoxyethyl) ether, 1,4-dioxane and thiophene, ketones, for example acetone; hydrocarbons, for example benzene, toluene, xylene and hexane; organic bases, for example pyridine; halogenated hydrocarbons and particularly chlorinated hydrocarbons, for example chlorobenzene, chloroform, carbon tetrachloride and methylene dichloride; amides, particularly tertiary alkylamides, for example dimethyl formamide; sulfoxides, for example dimethyl sulfoxide; sulphones, for example sulfolane; nitriles, for example acetonitrile; alcohols, for example ethanol; nitro compounds, for example nitropropane; and alkyl carbonates and sulphates, for example propylene carbonate and dimethyl sulphate. Polar aprotic solvents, especially dimethyl sulfoxide, are particularly suitable solvents in the case where a pyridyl tetrahydro (thio) pyran

PATENT SPECIFICATION

(11) 1310812

1310812

NO DRAWINGS

- (21) Application No. 26925/69 (22) Filed 28 May 1969
 (21) Application No. 45151/69 (22) Filed 12 Sept. 1969
 (21) Application No. 57392/69 (22) Filed 24 Nov. 1969
 (23) Complete Specification filed 8 May 1970
 (44) Complete Specification published 21 March 1973
 (51) International Classification G03C 1/72; C08G 33/02; C09K 1/02
 (52) Index at acceptance
 G2C C16 CX
 C3R 7N5A 7PX
 C4S 311 33Y 43Y 650 66Y 670 705 709 714 717
 735 753 76Y
 H1D 4F9 4HX 4HY 4K2A 4K2C 4K2Y 4K3B 4K9



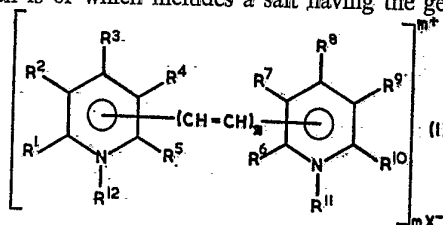
- (72) Inventors JOHN GRAHAM ALLAN, ERIC PAUL
 GOODINGS, TIMOTHY DOUGLAS ANDREWS,
 GLYN DAVID SHORT and IEUAN THOMAS

(54) RADIATION SENSITIVE MATERIALS CONTAINING NITROGENOUS CATIONIC COMPOUNDS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to radiation sensitive materials.

According to this invention we provide a radiation sensitive material comprising a polymeric film which is or which includes a salt having the general formula:



where

R^1 — R^{10} are hydrogen, halogen or organic substituents

R^{11} , R^{12} , if present, are halogen or organic substituents

$z=0$ or an integer

X^- is an anion derived from a strong acid of pKa less than 2.5

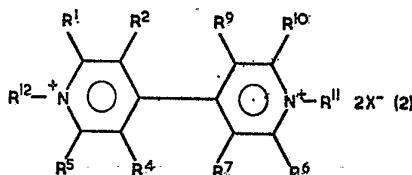
$m=1$ or 2

and at least one of the nitrogen atoms is quaternary.

Usually the link joins the two aromatic rings in the 4,4' or 2,2' positions, when it replaces $R^{3,8}$ or $R^{5,6}$, e.g. 2,2'-bipyridyls and 4,4'-bipyridyls.

Our copending British Patent Application No. 36409/71 (Serial No. 1,310,813) claims as new compositions of matter monomeric salts containing a N,N'-bis(p-cyano-phenyl)-4,4'-bipyridylium cation, which fall within the above general formula.

Pairs of substituents on the same or adjacent rings may be links to form cyclic structures. For example, in radiation sensitive components containing a 4,4'-bipyridyl structure (2).



NO DRAWINGS

- (21) Application No. 12175/69 (22) Filed 7 March 1969
 (61) Patent of Addition to No. 1 073 081 dated 8 April 1965
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 (45) Complete Specification published 18 Oct. 1972
 (51) International Classification C07D 31/22
 (52) Index at acceptance
 C2C 173—197—288 215 246 247 250 251 25Y 28X 290
 29Y 30Y 61X ZB
 (72) Inventors JOHN EDWARD COLCHESTER, JOHN GERARD
 CAREY and MICHAEL DAVID TAYLOR



(54) PRODUCTION OF BIS-QUATERNARY SALTS OF 4,4'-BIPYRIDYLS

- (71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 This invention relates to the production of 1,1' - disubstituted - 4:4' - bipyridylum salts.
- In U.K. Patent Specification No. 1,073,081 there is described a process for the production of N:N' - (or 1,1'-)disubstituted - 4:4'-bipyridylum salts by the oxidation of an N:N' - (or 1,1'-)disubstituted - tetrahydro-4:4'-bipyridyl using an organic oxidising agent which is a hydrogen acceptor and which has a redox potential in water more positive than -1.48 volts as compared with the standard calomel electrode.
- We have now found that N:N'-disubstituted - 1,1',4,4' - tetrahydro - 4:4' - bipyridyls may advantageously be converted to the corresponding bipyridylum salts by the use of particular oxidising agents which can be regenerated by oxygen.
- Thus according to the present invention we provide a process for the production of a 1,1' - disubstituted - 4:4' - bipyridylum salt which comprises treating a 1,1'-disubstituted-1,1',4,4' - tetrahydro - 4:4' - bipyridyl with a 2 - alkyl - 9,10 - anthraquinone, the 2-alkyl-9,10-anthraquinone being such that the corresponding 9,10-anthraquinol can be oxidised to the substituted 9,10-anthraquinone by oxygen and also being such that it is a hydrogen acceptor and has a redox potential in water more positive than -1.48 volts as compared with the standard calomel electrode.
- The substituted 9,10-anthraquinone preferably has no substituent on its alpha-carbon atoms as we have found that such substituents tend to slow the rate of reaction, possibly by steric hindrance of the 9 and/or 10 positions. If, however, alpha-substituents are present they should preferably be few and small if a high rate of reaction is required. The alkyl group of the substituted 9,10-anthraquinone preferably contains from 1 to 8 carbon atoms, especially 1 to 4 carbon atoms. Examples of particularly suitable alkyl groups which may be present are methyl, ethyl, *n*-butyl, *iso*-butyl and *tert*-butyl groups.
- The 1,1' - disubstituted - tetrahydro-4:4'-dipyridyl may be in particular a 1,1'-dialkyl - tetrahydro - 4:4' - bipyridyl or a 1,1' - dicarbamidoalkyl - tetrahydro - 4:4'-bipyridyl; the latter are more fully described in U.K. Patent Specification No. 1,073,082.
- The reaction may be conveniently carried out in solution in an inert solvent, especially an inert organic solvent which will dissolve both the 1,1' - disubstituted - tetrahydro-4:4'-bipyridyl and the 2-alkyl-9,10-anthraquinone. Examples of inert organic solvents which may be used are ethers, for example diethyl ether, tetrahydrofuran and bis(2-methoxy ethyl) ether; ketones, for example acetone and methyl ethyl ketone; hydrocarbons for example alpha- and beta- methyl naphthalenes, benzene and alkyl benzenes such as dodecyl benzene and those known in commerce as "Aramasols"; inert halogenated hydrocarbons, particularly chlorinated hydrocarbons, dimethyl formamide; alcohols, for example diisobutyl carbinol and long-chain fatty alcohols, for example palm kernel alcohol. Mixtures of any two or more organic solvents may be employed, especially mixtures of alpha-methyl naphthalene and diisobutyl carbinol or palm kernel alcohol; in these particular mixtures to solubility of the 2-alkyl-9,10-anthraquinone may be as high as 20% by weight of the resulting solution.
- The rate of reaction depends on the particular 2-alkyl-9,10-anthraquinone used and the

PATENT SPECIFICATION

(11) 1 259 840

NO DRAWINGS



1 259 840

- (21) Application No. 61010/68 (22) Filed 23 Dec. 1968
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 (45) Complete Specification published 12 Jan. 1972
 (51) International Classification C 07 d 31/22
 (52) Index at acceptance
 C2C 173—197—288 215 246 247 250 251 25Y 28X 29X 29Y
 30Y 61X ZB
 (72) Inventors JOHN EDWARD COLCHESTER,
 JOHN FRANCIS CAIRNS and JOHN GERRARD CAREY

(54) MANUFACTURE OF BIPYRIDILIUM SALTS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of bipyridylum salts and particularly to a process for the manufacture of 1,1'-disubstituted-4,4'-bipyridylum salts which are useful herbicides by oxidation of the corresponding 1,1'-disubstituted-1,1',4,4'-tetrahydro-4,4'-bipyridyl.

In U.K. Patent Specification No. 1,073,081 we have described and claimed a process for the production of an N,N'- (or 1,1'-) disubstituted-4,4'-bipyridylum salt by treating an N,N'-disubstituted-tetrahydrobipyridyl with an oxidising agent that is an organic compound which is a hydrogen acceptor and which has a redox potential in an aqueous system more positive than -1.48 volts with respect to the standard calomel electrode.

We have now found that a number of organic compounds can oxidise tetrahydrobipyridyls to yield intermediate oxidation products which are readily further oxidisable, for example by means of air, to bipyridylum salts. These intermediate oxidation products are 1,1'-disubstituted-1,1'-dihydro-4,4'-bipyridyls and we have found that suitable organic oxidising agents for forming them are agents which have a redox potential in an aqueous system more positive than -1.48 volts with respect to the standard calomel electrode and which accept a hydride ion (H^-) to form an unstable anion.

Oxidation of the tetrahydrobipyridyl is believed to occur initially by transfer of a hydride ion (H^-) therefrom to the oxidising agent to form an anion. Further oxidation

of the tetrahydrobipyridyl to a dihydrobipyridyl could then occur by transfer of a proton (H^+) from the product of the initial oxidation to the anion formed in the initial oxidation. The overall reaction is therefore believed to be a concerted ionic elimination of hydrogen. The intermediate anion is capable of effecting the transfer of a proton from the product of the initial oxidation and for the purposes of this specification is called an unstable anion. An alternative definition is that the anion is not able to be stabilised under the conditions of the reaction by a bipyridylum cation; such anions have a redox potential under the conditions of the reaction more negative than -0.45 volt with respect to the standard calomel electrode.

According to the present invention we provide a process for the manufacture of a 1,1'-disubstituted-4,4'-bipyridylum salt which comprises treating the corresponding 1,1'-disubstituted-1,1',4,4'-tetrahydro-4,4'-bipyridyl with an organic compound which has a redox potential in water more positive than -1.48 volts as compared with the standard calomel electrode and which accepts a hydride ion to form an anion which under the conditions of the reaction has a redox potential more negative than -0.45 volt with respect to the standard calomel electrode, and subsequently oxidising the resulting 1,1'-disubstituted-1,1'-dihydro-4,4'-bipyridyl by means of an oxidising agent which has a redox potential in water more positive than -0.50 volt as compared with the standard Calomel electrode.

The reaction may be carried out conveniently in a solvent, usually in an organic solvent, which will dissolve the N,N'-disubstituted tetrahydrobipyridyl and preferably also the oxidising agent. Suitable solvents include ethers, for example diethyl ether, tetrahydrofuran, 1,2-dimethoxy ethane, bis-(2-methoxyethyl) ether, and 1,4-dioxane;

[54] **MANUFACTURE OF BIPYRIDILIUM
SALTS**

[75] Inventors: **John Edward Colchester; John
Gerard Carey**, both of Runcorn,
England

[73] Assignee: **Imperial Chemical Industries
Limited**, London, England

[22] Filed: **Dec. 5, 1969**

[21] Appl. No.: **882,699**

[30] **Foreign Application Priority Data**

Dec. 20, 1968 Great Britain.....60,713/68

[52] U.S. Cl.....**260/295 AM, 260/296 D, 71/94**

[51] Int. Cl.....**C07d 31/44**

[58] Field of Search.....**260/295 AM, 296 D**

[56] **References Cited**

UNITED STATES PATENTS

3,405,135 10/1968 Colchester et al.260/295 AM

Primary Examiner—Alan L. Rotman
Attorney—Cushman, Darby & Cushman

[57] **ABSTRACT**

A process for the manufacture of a 1,1'-disubstituted-4,4'-bipyridylium salt which comprises treating the corresponding 1,1'-disubstituted-1,1',4,4'-tetrahydro-4,4'-bipyridyl with an organic compound which has a redox potential in water more positive than -1.48 volts as compared with the saturated calomel electrode and which reacts with a hydride ion with the formation of an anion which under the conditions of the reaction has a redox potential more positive than -0.45 volt as compared with the saturated calomel electrode.

10 Claims, No Drawings

Document is not available for ZA6906953 (A)

[54] **PRODUCTION OF BIPYRIDILIUM
SALTS AND RELATED COMPOUNDS**

- [75] Inventor: **John Edward Colchester**, Runcorn,
England
- [73] Assignee: **Imperial Chemical Industries
Limited**, London, England
- [22] Filed: **March 1, 1971**
- [21] Appl. No.: **119,893**

Related U.S. Application Data

- [63] Continuation of Ser. No. 811,249, March 27, 1969,
abandoned.
- [52] U.S. Cl. **260/295 AM, 260/296 D**
- [51] Int. Cl. **C07d 31/42, C07d 31/44**

[58] **Field of Search**.....260/296 D, 295 AM

[56] **References Cited**

UNITED STATES PATENTS

3,642,790 2/1972 Cairns.....260/296 D X

Primary Examiner—Alan L. Rotman
Attorney—Cushman, Darby & Cushman

[57] **ABSTRACT**

A process for the production of 1,1'-disubstituted-4,4'-bipyridylium salts which comprises reacting the corresponding 1,1'-disubstituted-1,1',4,4'-tetrahydro-4,4'-bipyridyl with a free radical compound.

4 Claims, No Drawings

PATENT SPECIFICATION

(11) 1242711

1242711

NO DRAWINGS

- (21) Application No. 16474/68 (22) Filed 5 April 1968
 (21) Application No. 25774/68 (22) Filed 29 May 1968
 (23) Complete Specification filed 19 March 1969
 (45) Complete Specification published 11 Aug. 1971
 (51) International Classification C 07 d 31/14
 (52) Index at acceptance

C2C B4A2 B4M

- (72) Inventors JOHN GERARD CAREY, JOHN FRANCIS CAIRNS,
 JOHN EDWARD COLCHESTER and
 JOHN HUBERT ENTWISTLE



(54) MANUFACTURE OF 1,1'-DISUBSTITUTED BIPYRIDILIUM SALTS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of bis-quaternary salts of 4,4'-bipyridyl and 2,2'-bipyridyl which are useful herbicidal compounds.

According to the present invention we provide a process for the manufacture of 1,1'-disubstituted - 4,4' - (or - 2,2' -) bipyridylium salts which comprises treating the corresponding 1,1' - disubstituted - 1,1',4,4' - (or 1,1', 2,2' -) tetrahydro - 4,4' - (or 2,2' -) bipyridyl with an inorganic oxyacid anhydride or a salt of a metal capable of existing in at least two valency states wherein the metal is in a higher valency state, the redox potential in water of the anhydride or the metal salt between different valency states of the metal being more positive than -1.48 volts as compared with the saturated calomel electrode.

The treatment can conveniently be carried out in the presence of an inert solvent, usually a solvent which will dissolve the disubstituted tetrahydrobipyridyl and preferably also the resulting bipyridylium salt. Advantageously the solvent is substantially immiscible with water. Suitable solvents include ethers and thioethers for example diethyl ether, tetrahydrofuran, 1,2 - dimethoxyethane, bis - (2 - methoxyethyl) ether, 1,4 - dioxane and thiophene; ketones, for example acetone; hydrocarbons, for example benzene, toluene, xylene and hexane; organic bases, for example pyridine; halogenated hydrocarbons, for example chlorobenzene, chloroform, carbon tetrachloride, methylene dichloride and trichloroethylene; amides, particularly tertiary alkylamides for example dimethyl formamide; sulfoxides, for

example dimethyl sulphoxide, sulphones, for example sulfolane; carbon disulphide; nitriles, for example acetonitrile; alcohols; nitro compounds, for example nitropropane; and alkyl carbonates and sulphates, particularly propylene carbonate and dimethyl sulphate. Alternatively if the oxidising agent is an inorganic oxyacid anhydride, an excess of the liquid anhydride may be provided to act as the solvent. Use of alcohols (including glycols) for example ethylene glycol, diethylene glycol, methanol, 2 - (2 - methoxy ethoxy) ethanol, ethanol and isopropanol tend, however, to lead to lower yields of the bisquaternary salts, especially where a metal salt is employed as oxidising agent.

Metal salts which can be used include salts of an inorganic acid, for example metal chlorides, sulphates, carbonates or nitrates. The metal salt may be in the hydrated form. Examples of suitable metal salts are cobalt dichloride, cobalt nitrate, cobalt nitrate hexahydrate, cobalt sulphate heptahydrate, copper chloride, copper sulphate pentahydrate, ferric sulphate, lead nitrate and cerium sulphate. Alternatively the metal salt may be a salt of an organic acid for example acetic acid. It is to be understood that the term metal salt for the purposes of this specification includes metal complexes such as bis - N,N' - disalicyllylethylenediamine - μ - aquodicobalt (II), commonly known as salcomine. In addition, when the reaction is carried out in solution, the metal salt or the metal ions thereof may form a chemical complex with the solvent. Examples of solvents which may result in chemical complexes with metal salts are nitriles, for example acetonitrile, and amides, for example formamide.

Inorganic oxyacid anhydrides which can be used should be capable of accepting hydrogen ions from the tetrahydrobipyridyl, and in addition they should have a redox potential in

(19)



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(51) Int. Cl:

(12)

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(21) Application number: 31932

(71) Applicant:

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(22) Date of filing: 31.03.1969

(72) Inventor:

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(54) PROCESS FOR THE PREPARATION OF 1,1'- DISUBSTITUTED-1,1'-DIHYDRO- BIPYRIDYL COMPOUNDS

(54) תהליך להכנת 1,1'-דיהידרו ביפירידיל-1,1'-דומונתמרים